OBSERVATIONS ON THE RARE EARTHS: STUDIES IN ION EXCHANGE

BY

DONALD DEE STARR

A. B., Olivet Nazarene College, 1944
A. M., University of Illinois, 1946

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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I. Introduction

Ion exchange has been defined as the reversible interchange between a liquid phase and a solid body which does not involve any radical change in the structure of the solid (5). Reactions involving ion exchange in synthetic organic cation exchangers have been shown to be metathetical, and they are governed by the laws of mass action.

Separation of rare earth elements has been made possible by means of an ion exchange process. A variety of methods for separating the rare earths have been investigated. Fractional crystallization and basicity methods have been widely used for many years to this end. The only rapid and efficient separations have involved oxidation and reduction procedures for the separation of specific ions. Many methods for the separation of isotopes have not been applied to the rare earth separations because of the lack of stable gaseous or volatile compounds. Taylor and Urey (4) found that lithium and potassium isotopes could be fractionally concentrated by means of exchange reactions in long columns of ion exchangers. Russell and Pearce (1) applied this method to the partial fractionation of the yttrium earth elements. They found that the rare earth ions of decreasing crystal ionic radii were held more firmly in the zeolite lattice.

It was proposed to investigate further the behavior of rare earth ions with ion exchange materials in static equilibrium and dynamic systems.

II. Rare Earth Ion Exchange in Static Systems

Two important factors which affect the exchanging power of a cation are its charge and its size. The rare earth ions studied were all of oxidation state three; however, the ions

have different ionic crystal radii. Corresponding differences would be predicted among these elements in their "hydrodynamic" radii, i. e., the radii of the hydrated ions.

Solutions (0.1 M.) of lanthanum nitrate, neodymium nitrate, and yttrium nitrate were placed in contact with Amberlite IR-100 H, a phenol-formaldehyde resin containing hydrogen ions; Zeo-Karb Na, a carbonaceous zeolite with exchangeable sodium ions; and Super Zeo-Dur Na, a treated glauconite type greensand with exchangeable sodium ions. A comparison of the rare earth contents of the solutions after intervals up to two hours in length showed only small differences in the order of preference of the rare earths by the exchanger. Similar experiments were conducted with equimolar mixtures of yttrium and lanthanum, yttrium and neodymium, and lanthanum and neodymium in contact with Amberlite IR-100 H. The order of preference of the elements by the resin under these conditions was Nd > La > Y, but again the differences were small with little separation being effected.

III. Rare Earth Ion Exchange in Dynamic Systems

Boyd's method of selectively eluting ions from a column of an ion exchanger by passing through it ammonium citrate-citric acid solutions was found useful in the separation of yttrium from cerium and neodymium from praseodymium (2) (3). This process has been compared with the chromatographic separation of organic compounds. The rare earth ions are initially exchanged at the top of the long column of Amberlite IR-100 H. A solution of a citric acid-ammonium citrate mixture is passed through the column to selectively elute the ions, or "develop" zones of rare earths, by recurring ion in the resin-ion in solution exchanges. Two reactions are placed in competition:

$$(1 \qquad R_E^{+++} + 3R^- \rightleftarrows R_ER_3$$

$$(2 \qquad R_E^{+++} + (HC_6H_5O_7)^= \rightleftarrows [R_E(HC_6H_5O_7)]^+$$

Where R^- represents the anion in the Amberlite resin.

The second reaction is by far the more important in effecting separation of the rare earth elements. The ion forming the more stable citrate complex is moved down the column in the leading fractions.

Neodymium-Cerium Mixtures

Neodymium was found to be removed in preference to cerium by this method. The pH of the elutriant, the flow rate of the elutriant, the particle size of the exchanger, and the amount of rare earth in contact with the exchanger were varied in an effort to improve the separation of the mixtures.

A 5% solution of citric acid was ineffective in the removal of rare earth from an Amberlite column. Addition of ammonia to the elutriant increased the pH of the solution and the concentration of the acid citrate ion which complexes with the rare earth ion, as well as providing ammonium ions to remove the rare earth from the exchange points. The time for elution of the rare earth was prohibitive when elutriants of low pH were used. As the pH of the elutriant was increased from 2.6 to 2.8, the separation decreased. Elutriants of high pH removed the rare earth from the column too rapidly to achieve any separation.

As the flow rate of the elutriant through the column was decreased the separation of neodymium from cerium was increased. At the slower rate of flow, more ion in the resin-ion in solution exchanges were possible, consequently improved separation resulted.

Better separation was achieved as the amount of rare earth per square centimeter of cross sectional column area was decreased. The smaller amount of rare earth was held by a shorter length of resin in the initial exchange at the top of the column, leaving a longer length of column on which fractionation might occur. With a shorter length of resin used in the initial exchange, the neodymium ions at the back of the area had a shorter distance to be moved past

the cerium ions to the neodymium "zone," with more separation resulting.

By using smaller particles of Amberlite in the column the separation of neodymium from cerium was markedly improved.

Under equivalent conditions yttrium was removed much more readily from cerium than neodymium from cerium.

Lanthanum-Cerium Mixtures

Using the method above, the cerium was removed in preference to the lanthanum. Improvements in separation were achieved by using elutriant of a lower pH and by passing the elutriant through the column at a slower rate of flow.

Lanthanum-Cerium-Neodymium Mixtures

A lanthanum-cerium-neodymium mixture containing the elements in amounts approximating a natural mixture (1:4:2) was selectively eluted through a column of Amberlite IR-100 H. The elements were removed in the order of decreasing atomic number, neodymium, cerium, and then lanthanum.

IV. Summary

Only small differences were observed among lanthanum, neodymium, and yttrium ions in their exchange with Amberlite in static systems. Separation of rare earth mixtures was accomplished by selective elution of the ions from an

Amberlite column by means of a citric acid-ammonium citrate elutriant. Increased separation was achieved by decreasing the pH of the elutriant, the flow rate of the elutriant, the amount of rare earth used, and the particle size of the exchanger and by increasing the length of the column.

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VITA

Donald Dee Starr was born in Marlette, Michigan, on October 4, 1922. He attended the public schools in Michigan, and in 1939 he was graduated from Muskegon Senior High School, Muskegon, Michigan. He received the degree of Bachelor of Arts in Chemistry, magna cum laude, from Olivet Nazarene College, Kankakee, Illinois, in 1944. He entered the Graduate School of the University of Illinois in October, 1944, and was granted the degree of Master of Arts in Chemistry in February, 1946. He held an appointment as half-time teaching assistant in inorganic chemistry from October, 1944, until June, 1946. From that time until September, 1947, he was a research assistant on the University of Illinois Rare Earth Research Program sponsored by the Office of Naval Research.

He is a member of the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, and Alpha Chi Sigma.